Flux Synthesis of $K_2Cu_2P_4Se_{10}$: A Layered Selenophosphate with a New Cyclohexane-like $[P_4Se_{10}]^{4-}$ Group

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The A/P/Q (A = alkali metal; Q = S, Se) flux provides essentially a solution medium where $[P_yQ_z]^{n-}$ anions can exist in high concentrations, their identity and character depending on the alkali polychalcophosphate basicity and composition. Each $[P_yQ_z]^{n-}$ anion can form, grow, and disappear, or convert inside the flux, and therefore it presents itself as a classical coordination ligand for metal ions.[1−6] The polychalcophosphate flux method has afforded several new $[P_yQ_z]^{n-}$ anions which serve as building blocks in novel compounds such as $A_5Sn(PSe_5)_3$ (A = K, Rb),[2d] $Rb_4Ti_2(P_2Se_9)_2(P_2Se_7)$,[3b] $K_3RuP_5Se_{10}$,[3e] and $A_3AuP_2Se_8$ (A = K, Rb, Cs).[3f]

The dissolution of Cu in A/P/Se fluxes has given two phases: one with Cs and one with K. Both phases have the same empirical formula, but a strong counterion effect enforces two different structures on them. The one-dimensional $Cs_2Cu_2P_2Se_6$[3a] features trigonal planar copper atoms, with $Cu^+\cdots Cu^+$ interactions bridged by the ethane-like $[P_2Se_6]^{4-}$ group, whereas $K_3Cu_3P_3Se_9$[5] has a three-dimensional network with tunnels running along the *a* and *b* directions. Its framework is also built with $[P_2Se_6]^{4-}$ anions. The only other related phases are Cu_3PSe_4[7a] and quaternary $CuMP_2Se_6$ (M = Cr, In),[7b] which have been prepared by direct combination reactions. Further investigations into the Cu chemistry in the aforementioned fluxes led to $K_2Cu_2P_4Se_{10}$, a new phase with an unprecedented cyclohexane-like $[P_4Se_{10}]^{4-}$ group.

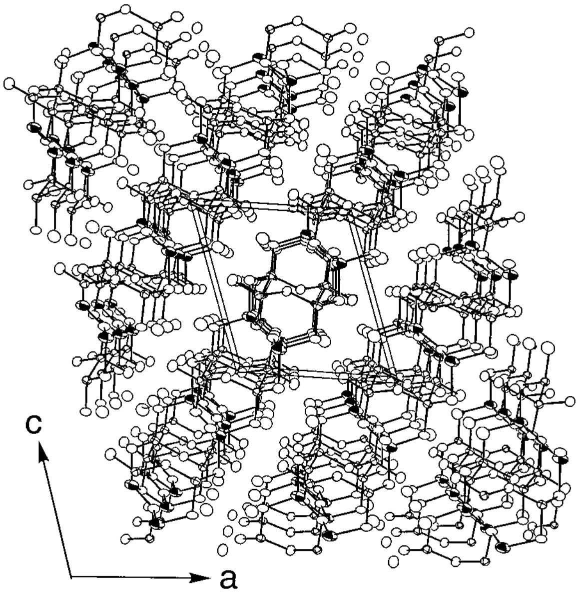

Figure 1. Structure of $K_2Cu_2P_4Se_{10}$ viewed down the *b* axis. K^+ ions are light gray ellipsoids, selenium atoms are open ellipsoids, and phosphorus atoms are small black ellipsoids.

$K_2Cu_2P_4Se_{10}$[8] is a compound with a new, two-dimensional structure type. It contains $[Cu_2P_4Se_{10}]_n^{2n-}$ layers which are separated by eight-coordinate K^+ cations [range of K−Se distances 3.396(3)−3.780(3) Å; average 3.528 Å], as shown in Figure 1. The layers consist of infinite chains of corner-sharing $CuSe_4$ tetrahedra that propagate along the *b* axis; see Figure 2A. These chains are then interstitched in two dimensions by cyclic $[P_4Se_{10}]^{4-}$ groups. The latter are observed for the first time and feature P−P bonds with tetravalent P atoms. The only other $[P_yQ_z]^{n-}$ group with P−P bonds and P^{4+} is the ethane-like $[P_2Se_6]^{4-}$. The $[P_4Se_{10}]^{4-}$ group forms a cyclohexane-like ring with the chair conformation, which consists of four phosphorus and two selenium atoms; see Figure 2B. It can be viewed as the result of a fusion between two $[P_2Se_6]^{4-}$ groups which share two common selenium atoms [Se(3), Se(3′)]. As a ligand, it possesses eight terminal Se atoms available for coordination. In the present case, the unit utilizes six terminal Se atoms to engage four Cu atoms to build the entire $[Cu_2P_4Se_{10}]_n^{2n-}$ layer; see Figure 2B.

The Cu atoms have tetrahedral coordination with Cu−Se distances averaging 2.46(5) Å, similar to those found in $Cs_2Cu_2P_2$-

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(8) (a) $K_2Cu_2P_4Se_{10}$ was synthesized from a mixture of Cu (0.30 mmol), P (0.90 mmol), K_2Se (0.30 mmol), and Se (2.40 mmol) which was sealed under vacuum in a Pyrex tube and heated to 570 °C for 2 d, followed by cooling to 50 °C at 21 °C h^{-1}. The excess $K_xP_ySe_z$ flux was removed with degassed DMF. Further washing with anhydrous ether revealed red, irregularly shaped crystals of $K_2Cu_2P_4Se_{10}$ (~88% yield based on Cu). The crystals are air- and water-stable. Semiquantitative microprobe analysis on single crystals gave $K_{1.9}Cu_2P_{4.2}Se_{10.7}$ (average of four data acquisitions). (b) A Rigaku AFC6S diffractometer equipped with a graphite crystal monochromator and Mo Kα (λ = 0.710 69 Å) radiation was used to collect data from a crystal of dimensions 0.22 × 0.11 × 0.08 mm in the $\omega-2\theta$ scan mode. The structure was solved with SHELXS-86[9a] and refined by full-matrix least-squares techniques of the TEXSAN[9b] software package. Crystal data at 23 °C: a = 10.627(2) Å, b = 7.767(1) Å, c = 11.966(1) Å, β = 109.125(8)°, V = 933.2(2) Å^3, Z = 2, D_c = 3.981 g cm^{-3}, space group $P2_1/n$ (No. 14), μ(Mo Kα) = 225.52 cm^{-1}, $2\theta_{max}$ = 50.0°, octants collected $0 < h < 13$, $0 < k < 9$, $-14 < l < 14$; number of total data collected 1888; number of unique data 1787 (R_{int} = 0.024); number of data with $F_o^2 > 3\sigma(F_o^2)$ 1145; number of variables 82. An empirical absorption correction based on ψ scans was applied to the data; absorbance ratio (min/max) 0.7831. All atoms were refined anisotropically. Final R/R_w = 0.028/0.027.

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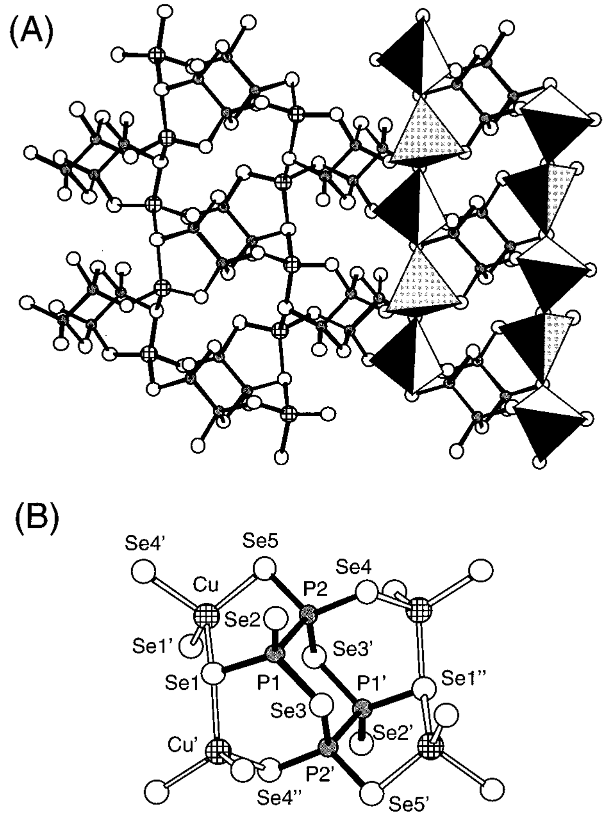

Figure 2. (A) A single $[Cu_2P_4Se_{10}]_n^{2n-}$ layer viewed in the $[\bar{1}01]$ direction. Some corner-sharing $CuSe_4$ tetrahedra are shown in polyhedral representation. (B) A fragment of the same layer with labeling. Selected distances (Å): Cu−Se(1) 2.488(2), Cu−Se(1′) 2.524(2), Cu−Se(4) 2.450(2), Cu−Se(5) 2.394(2), P(1)−Se(1) 2.186(3), P(1)−Se(2) 2.138(3), P(1)−Se(3) 2.277(3), P(2)−Se(3′) 2.281(3), P(2)−Se(4) 2.151(3), P(2)−Se(5) 2.161(3), P(1)−P(2) 2.246(4). Selected angles (deg): Se(1)−Cu−Se(1′) 109.88(5), Se(1)−Cu−Se(4) 112.32(7), Se(1)−Cu−Se(5) 110.39(6), Se(1)−P(1)−P(2) 109.2(1), similar angles around P(2), P(1)−Se(3)−P(2′) 109.9(1), P(1)−Se(1)−Cu 96.36(8), P(2)−Se(5)−Cu 94.72(8), Cu−Se(1)−Cu′ 143.33(6), P(2′)−Se(4″)−Cu′ 102.61(9).

Se_6[3a] and $K_3Cu_3P_3Se_9$[5]. Selected distances and angles are given in the caption of Figure 2. The P−Se distances range from 2.138(3) to 2.281(3) Å, with the noncoordinated selenium atoms [Se(2)] displaying the shorter ones.

The stabilization of the new $[P_4Se_{10}]^{4-}$ anion, instead of the very common $[P_2Se_6]^{4-}$, perhaps can be rationalized in terms of flux Lewis basicity. The composition of the flux (Cu:P:K_2Se:Se = 1:2:1.5:4.5),[10] used to obtain $K_3Cu_3P_3Se_9$,[5] has a Lewis bacisity which typically favors the formation of the $[P_2Se_6]^{4-}$ anion (P^{4+}).[3f] In the case of $K_2Cu_2P_4Se_{10}$, the composition (Cu:P:K_2Se:Se = 1:3:1:8) contains less K_2Se and more Se, thus rendering the flux even less basic and this presumably forces the $[P_2Se_6]^{4-}$ anion to convert to the $[P_4Se_{10}]^{4-}$ anion according to the equilibrium shown in eq 1.

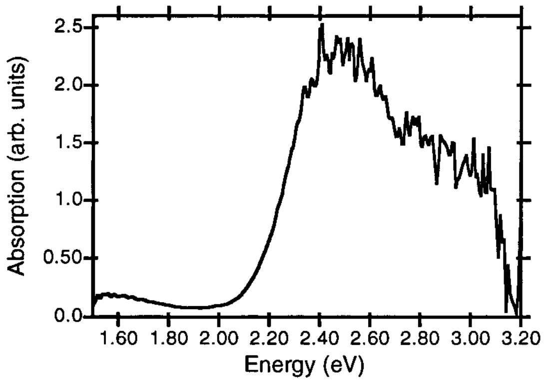

Figure 3. Single-crystal absorption spectrum of $K_2Cu_2P_4Se_{10}$.

$$2[P_2Se_6]^{4-} \rightleftharpoons [P_4Se_{10}]^{4-} + 2Se^{2-} \qquad (1)$$

Single-crystal optical transmission measurements on transparent, well-formed crystals give the spectrum of Figure 3, which shows a sharp gap, E_g, of 2.07 eV. Therefore, the compound is a semiconductor. The infrared spectrum displays absorptions at ca. 499 (vs), 488 (vs), 479 (vs), 435 (s), 387 (vs), 302 (vs), 194 (m), and 159 (m) cm^{-1}. These vibrations are very similar to the ones observed for the $[P_2Se_6]^{4-}$ group.[3a,c] The absorptions below 200 cm^{-1} are most probably due to Cu−Se vibrations.[3] Differential thermal analysis (DTA) suggests that $K_2Cu_2P_4Se_{10}$ melts congruently at ca. 470 °C.

The synthesis of $K_2Cu_2P_4Se_{10}$ was accomplished through the chalcophosphate flux method. With this compound, the repertoire of chalcophosphate ligands is expanded to include the new cyclohexane-like $[P_4Se_{10}]^{4-}$ unit. The latter is the only other anion, except $[P_2Se_6]^{4-}$, which contains P−P bonds and P^{4+}. It would be interesting to see if the $[P_4Se_{10}]^{4-}$ unit can be isolated as a molecular species, using charge-balancing alkali metal cations [e.g., $A_4P_4Se_{10}$ (A = K, Rb, Cs)].[11]

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Supporting Information Available: Tables of crystal data and X-ray experimental details, fractional atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all atoms, interatomic distances and angles, and calculated and observed X-ray powder patterns (16 pages). Ordering information is given in any current masthead page.

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[10] The actual flux composition[5] was 1.5:0 of K_2Se_4:Se, which is equivalent to 1.5:4.5 of K_2Se:Se.

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